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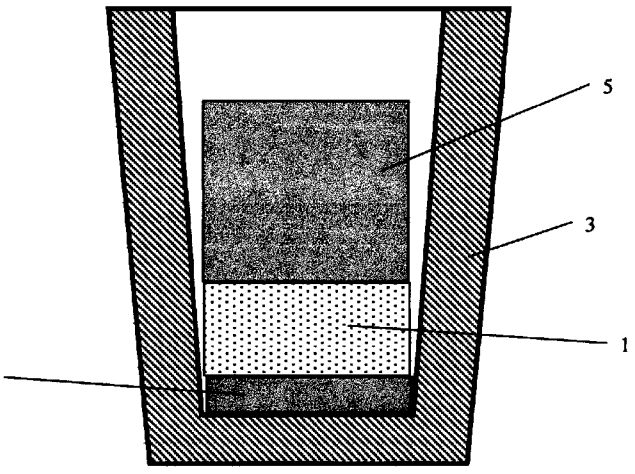
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(54) Title: METHOD FOR PRODUCING ALUMINUM MATRIX COMPOSITES THROUGH PRESSURELESS INFILTRATION

Fig. 1



(57) Abstract: The present invention deals with the production of aluminum matrix composites through pressureless infiltration, where a preform, made from the mixtures of at least one kind of reinforcements materials and aluminum or aluminum alloy powder, is spontaneously infiltrated by molten matrix aluminum or aluminum alloys under a protective environment, at a temperature ranging from 700 °C to 1500 °C.

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METHOD FOR PRODUCING ALUMINUM MATRIX COMPOSITES THROUGH PRESSURELESS INFILTRATION

The present invention refers to a method for producing aluminum matrix composites through pressureless infiltration.

Aluminum matrix composites possess high specific stiffness and specific strength, good high temperature properties, fine fatigue and wear resistance, good damping capacity and low thermal expansion coefficient. As any other composite, they can combine specific mechanical and physical properties to satisfy requirements of application. Accordingly, aluminum matrix composites have become one of the most common and important metal matrix composites.

Aluminum matrix composites are usually fabricated by the process of squeeze casting, powder metallurgy, pressure infiltration, stirring casting and pressureless infiltration or spontaneous infiltration. Among them, pressureless infiltration processing has a greater potential for

industry application for its simple process, low cost and since it has no limitation on the size or shape of the products. The main shortcoming for this processing is its application scope. The application of pressureless infiltration is highly reliable on the wettability between reinforcement material and molten aluminum or aluminum alloys, while usually the wettability is relatively poor for the common used ceramic reinforcement (such as alumina) and molten matrix aluminum or aluminum alloys. There are three main kinds of methods to improve the wettability so as to induce the infiltration spontaneously: one is through altering the component of the matrix by adding some alloying elements (e.g. magnesium or lithium are commonly applied on this purpose); another is by modifying the surface properties of the reinforcement with coating infiltration enhance agent (e.g. nickel or titanium nitride) on its surface or forming some infiltration enhancer (e.g. magnesium aluminate spinel or aluminum nitride) at the interface between reinforcement and matrix; the other is by changing the reinforcement or matrix metal into another, while introducing a reaction before or along with the infiltration, which is also defined

as reactive infiltration. Besides, a special pressureless infiltration can be generated by providing vacuum atmosphere or forming inner vacuum with consuming reactive inner gas.

US-A-5509555 discloses a method of producing an article by pressureless reactive infiltration. In this invention, a porous preform containing at least carbon can be infiltrated by a liquid infiltrant alloys containing at least two elements among Al and Si or Cu and Si. Wetting is achieved along with the infiltration process thanks to the formation of silicon carbide. There are limits on the component of the preform (it must contain carbon) and on the infiltrating alloys (Al-Si or Cu-Si), which restricts greatly its application. Besides, the temperature required in US-A-5509555 is relatively high (900 °C-1800 °C), usually higher than 900 °C, resulting in a high cost of production.

EP-A-0291441 describes a method of making a aluminum matrix composite by spontaneous infiltration of a permeable mass of ceramic filler material with a molten aluminum. Where matrix aluminum alloy contains at least about 1 weight percent magnesium, under an atmosphere condition

containing about 10 to 100% by volume of nitrogen, balance non-oxidizing gas is in the range from 700 °C to 1200 °C, where the aluminum matrix composites produced typically contain aluminum nitride in the aluminum matrix as a discontinuous phase, which is formed during the infiltration thanks to the reaction between the aluminum matrix (also thanks to the presence of magnesium) and the nitrogen atmosphere, and is believed to have a positive effect on the spontaneous infiltration. The required control of atmosphere and the component of matrix alloy make the process complex, increase the cost of production and limit the application (only a magnesium-containing aluminum alloy can serve as matrix).

EP-A-0115742 discloses a composite structural electrolytic aluminum-production cell component with the structure of a ceramic preformed matrix infiltrated by aluminum. It provides one way to render the non-wettable material (such as alumina) wettable by molten aluminum through pre-coating a wetting agent on its surface. And the wetting agent can be chosen among lithium, magnesium, calcium, titanium, chromium, iron, cobalt, nickel, zirconium or hafnium and the diborides of titanium,

zirconium, hafnium and niobium. However, the pre-coating process would greatly increase the cost of equipment and production. Besides, the required temperature is usually too high (with Ni coating, 1200 °C for 12 hours) so that it is not suitable for commercial application.

EP-A0368784 discloses a method of fabricating metal matrix composites by spontaneously infiltrating the filler material or preform with molten matrix metal, where the infiltration is believed to be induced by the communication between infiltrating atmosphere and filler material, or preform or matrix metal, which would supply some infiltration enhancer or infiltration enhancer precursor at the interface between matrix and filler. As a development of EP-A-0291441, the present invention significantly broaden the application. The point is at the presence of nitrogen together with an infiltration enhancer precursor such as magnesium/strontium or at the presence of oxygen together with zinc/calcium, the matrix aluminum melt can spontaneously infiltrate the filler. Similar to EP-A-0291441, wetting occurs along with the infiltration during forming infiltration enhancer. The required control of

atmosphere and the component of matrix alloy make the process complex, increase the cost of production and limit the application.

EP-A-1178127 discloses a method for producing metal-based composite by pressureless infiltration without control of atmosphere. In this patent, infiltration-accelerating metal (magnesium) and reinforcing filler (silicon carbide) are charged into an aluminum container with 30%-70% of space filled with air, then the aluminum container is sealed and melted in a matrix metal melt. After infiltration, by solidifying the matrix metal melt and portion of the matrix metal a composite is produced. In this patent, sealed aluminum container with residual air inside generates a pressure at high temperature which contributes to the initial infiltration, the reaction products of magnesium and air improve the wetting and contribute to the final infiltration. Similar to EP-A-0368784 and EP-A-0291441, the presence of nitrogen/oxygen and infiltration enhancer precursor are required, while in this invention, a sealed aluminum container with 30%-70% of air is provided to control the atmosphere which could simplify the process and reduce the production cost. However, in EP-A-

1178127, the composite produced is cooling along with the matrix melt, which makes it difficult for it to be separated from the solidified matrix. Similar to EP-A-0368784, with the presence of oxygen and nitrogen, an infiltration-accelerating metal is selected from metal containing magnesium, calcium or zirconium. The addition of this kind of infiltration-accelerating metal would probably alter the final component on the matrix material.

Purpose of the present invention is solving the above prior art problems; to simplify the process, flexibly control the reinforcement percentage and further extend the application scope of pressureless infiltration technology, a new approach of fabricating aluminum matrix composites is provided in the current invention, wherein most of reinforcement materials like oxides (alumina, silica, etc), carbides (SiC, TiC, B_4C, etc), borides (TiB_2, AlB, MgB_2), nitrides (AlN, TiN, Si_3N_4) can be pressureless infiltrated by molten aluminum or aluminum alloys at temperature range of 700 °C-1500 °C, with mixing them with sufficient amount of aluminum or aluminum alloys powder, in a protective environment such as Nitrogen, Argon or Vacuum atmosphere.

The above and other objects and advantages of the invention, as will result from the following description, are obtained with a method for producing aluminum matrix composites through pressureless infiltration as claimed in Claim 1. Preferred embodiments and non-trivial variations of the present invention are the subject matter of the dependent claims.

It is intended that the enclosed claims are an integral part of the present description.

The present invention will be better described by some preferred embodiments thereof, provided as a non-limiting example, with reference to the enclosed drawings, in which:

- Figure 1 is a schematic, side sectional view of a crucible in which Example 1 of the method of the present invention can be carried out;

- Figure 2 is a schematic, side sectional view of a crucible in which Example 2 of the method of the present invention can be carried out; and

- Figure 3 is a schematic diagram of the main steps of the method according to the present invention.

With reference to the Figures, a preferred embodiment of the method for producing aluminum

matrix composites through pressureless infiltration method of the present invention is shown and described. It will be immediately obvious that numerous variations and modifications (for example related to shape, sizes, arrangements and parts with equivalent functionality) can be made to what is described, without departing from the scope of the invention as appears in the enclosed claims.

In the method of this invention, a permeable mass or preform comprising at least one kind of reinforcement and aluminum or aluminum alloys powder can be infiltrated by molten aluminum or aluminum alloy in a protective environment without extra pressure. The reinforcement materials comprise oxides (alumina, silica, etc.), carbides (SiC, TiC, B_4C, etc.), borides (TiB_2, AlB, MgB_2, etc.), nitrides (AlN, TiN, Si_3N_4, etc.). Said aluminum powder can be the same as a matrix metal or different from a matrix metal as component. A sufficient amount of aluminum is required for a good infiltration and the amount depends on the properties of the reinforcement, the aluminum powder and the formed preform, and also on the infiltration temperature, since the dimension of the reinforcement and aluminum powder and the

porosity of the preform have an evident influence on the infiltration. Generally speaking, a higher temperature, a larger reinforcement dimension and a lower preform porosity would have a positive influence on the infiltration.

After a sufficient infiltration, the derived composites can be taken out directly from a molten aluminum bath at a relatively low temperature (about 680 °C), and cooled with air, or they can be cooled down along with the molten aluminum bath with a furnace, and then be cut out from the solidified remains.

Summarising, the inventive method for producing aluminum matrix composites through pressureless infiltration, comprises the steps of:

- preparing, as pre-wettability, a permeable mass/preform comprising at least one type of reinforcement and aluminum or aluminum alloys powder; and
- communicating reinforcement and aluminum powder to generate a spontaneous infiltration of said permeable mass/preform with molten matrix aluminum or aluminum alloys in a protecting environment at an infiltration temperature without extra pressure.

In particular, it is provided that the step of preparing as pre-wettability comprises the substeps of:

- weighing the reinforcement;
- weighing the aluminum or aluminum alloys powder;
- mechanically mixing reinforcement and aluminum or aluminum alloys powder;
- making a green preform; and
- heating the green preform in a protecting environment.

Still particularly, the step of mechanically mixing is alternatively performed as:

- dry mixing, which generates mixture powders; or
- humid mixing, which generates a mixture with solvent, alternatively subjected to drying to obtain mixture powders or to pressing or tape casting.

Moreover, the following steps are provided:

- providing massive aluminum;
- immersing the green preform in an aluminum bath;

- pressureless infiltrating at a temperature ranging between 700 and 1500 °C;
- forming a composite in the aluminum bath;
- extracting the composite and cooling(or cooling within the matrix bath);
- obtaining the composite(or cutting out the composite).

The present invention will be described below using some non-limiting Examples of the method for producing aluminum matrix composites through pressureless infiltration.

Example 1

In this case 100mesh alumina powder and -325 mesh 6061 aluminum alloy powder were mixed in a solution of ethanol, with a weight ratio of 6:8:10. Low speed ball milling of the mixture was performed for 2 hours, then the suspension was transferred to a clean beaker. After a 30-minute standing, the sediments were taken out and heated and stirred at 80 °C for 30 minutes, until all the remained ethanol evaporated. In this way, a mixture of alumina and 6061-aluminum alloy powders was prepared. Cold isostatic pressing was applied with a pressure between 150 MPa-200 MPa, and a preform was obtained with a porosity of about 20%. A

coating was prepared in a refractory crucible (alumina) with a layer of fine alumina powder, and it was put inside the preform and two 6061 aluminum alloy masses with one of the mass on the top, another one on the bottom (Figure 1). The crucible was put into a furnace and the furnace was ventilated with inert Argon to form a protective atmosphere. The furnace was heated with a rate of 300-400 °C/h for 3-4 hours until it reached 1200 °C, holding the temperature for 2 hours. After infiltration, the furnace was cooled down to room temperature, then the application of argon gas was stopped and the crucible was taken out, finally cutting out the derived composites from the remains inside the crucible. Al_2O_{3p}/6061Al composites by pressureless infiltration were obtained.

Example 2

In this case, titanium diboride powder with dimension of 2-10 microns and -325 mesh 2024 aluminum alloy powder were mixed by stirring in a solution of butanol at room temperature for 2 hours. The weight ratio of the three components (TiB_2: 2024-Al: Butanol) was 1: 1: 2. After stirring, the suspension was left standing for 30 minutes until sedimentation occurred. The liquid

top layer was removed and the remains were stirred at 80 °C for another 30 minutes, till all liquid was removed. The mixture powders were subjected to cold isostatic pressing to get a preform with a pressure of 150-200 MPa; the porosity of the preform was about 25%-30%. The preform and matrix 2024 aluminum alloys were arranged into refractory crucibles as shown in Figure 2. The crucible was put into a furnace and the furnace was ventilated with nitrogen gas to form a protective atmosphere. The furnace was heated at the infiltration temperature of 700 °C with a heating rate of 300-400 °C for about 2 hours, holding the temperature at 700 °C for other 2 hours to generate the infiltration. After infiltration, the furnace was cooled down to 680 °C in 30 minutes, and the temperature was held for other 30 minutes. Then the application of nitrogen gas was stopped, fetching the derived composites and cooling it down in air. TiB_{2p}/2024 Al composites by pressureless infiltration were obtained.

Example 3

In this case, titanium carbide powder with particle size of 2-10 microns and -325 mesh 7075 aluminum alloys powder were mixed by stirring in a

solution of ethanol. Their weight ratio (TiC : 7075 : ethanol) was 19: 1: 10; the stirring process lasted 2 hours at room temperature to insure a good mixing of the mixture powder. The suspension was left standing for 30 minutes for sedimentation, then the top liquid layer was removed and the stirring process was continued for another 30 minutes at 80 °C to insure the complete evaporation of residual ethanol. After having obtained a good mixed mixture of titanium carbide and 7075 aluminum alloys powder, a process of cold isostatic pressing was applied to prepare the preform. With a pressure of 250 MPa - 300 MPa, the obtained preform had a porosity of around 35%-40%. The preform stuck in the middle of two 7075 aluminum alloys bulks was arranged inside of a refractory crucible and placed in a high temperature furnace. Vacuum atmosphere was required and a heating rate of 600 °C/hour was started when the vacuum degree was under 0.01 pascal. The temperature was held at 1100 °C for 2 hours, and the furnace was substantially cooled down to room temperature. Finally, TiC_p/7075 Al composites were obtained by cutting off the connected aluminum.

Example 4

UF10 silicon carbide powder and -325 mesh Al-Si10% powder with weight ratio of 5:1 were mixed by low speed ball milling along with butanol for about 2 hours. The suspension was taken out into a beaker for sedimentation leaving it stand for 30 minutes. After having removed the top butanol layer, the mixture sediment was heated and stirred at 80 °C for other 30 minutes to evaporate the remaining butanol, till the mixture was completely dry. Isostatic pressing was applied to the well mixed powder under a 200 MPa - 250 MPa pressure at ambient temperature and the porosity of the obtained preform was about 34%-38%. The preform was put in the middle of two Al-10Si alloys bulks, arranging them inside a refractory crucible and then heating them to 1000 °C with a high temperature furnace in an argon protective atmosphere. The heating rate was about 300-400 °C/h and after holding at 1000 °C for 2 hours, the furnace was cooled down to ambient temperature. The derived composites were cut out from the solidified remains and SiC_p/Al(Si) was obtained.

Example 5

In this case -325 mesh silicon powder and -325 mesh aluminum powder with a weight ratio of 1:10

were added into a mixture solvent of ethanol, butanol and fish oil. The suspension was mixed with some polyvinyl butyral (PVB) binder and polyethylene glycol (PEG) through low speed ball milling for 12 hours. Chopped silicon carbide fibers with 12 micron in diameter and 10mm in length were gradually added into the stirred slurry from a ball milling jar. The slurry was kept stirred for other 6 hours, then gas bubbles were removed from the slurry by reducing the air pressure. Tapes were made on a Tape Caster instrument with the final slurry. The air-dried tapes were firstly wetted with a mixture solvent of polyvinyl alcohol (PVA), ethanol and butanol; and then stacked to form a bulk. The preform was obtained by degreasing the bulk in an oven at a temperature of 500 °C protected by inert argon gas. Two bulks of Al-10Si alloys were sandwiched with the prepared preform and arranged into a refractory crucible inside an oven protected by inert argon gas. The oven temperature was raised at a rate of about 300-400 °C/h for 2-3 hours, and was held at 900 °C for 2 hours until infiltration completed. The oven was cooled down to room temperature, the connected aluminum was separated, and SiC_{sf}/Al-10Si

composites were obtained.

Example 6

In this case, a silicon carbide whisker with dimension of 1.5 micron in diameter and approximately 18 micron in length was used as reinforcement. The silicon carbide whisker was stirred with -325 mesh Al-10Si aluminum alloys for 2 hours to make them well mixed; their weight ratio was 10:1. The preform was prepared from the mixture through isostatic cold pressing with a pressure of 200-250 MPa and the preform porosity was around 25%. The preform was infiltrated similarly to what is described in Example 5, except that the infiltrating temperature was 850 °C. The furnace was cooled down to room temperature, the remains were taken out in the crucible, the connected aluminum was separated, and SiC_w/Al-10Si composites were obtained.

Example 7

A titanium nitride powder of a 2-10 micron size was mixed with 2219 aluminum alloys with a weight ratio of 3:2 through stirring for 2 hours. After being thoroughly mixed, the powder mixture was cold pressed to form a preform through isostatic pressing under a 200-250 MPa pressure,

and the preform porosity was around 30-35%. The preform was infiltrated similarly as Eample 2, except that the infiltration temperature was 750 °C and the matrix alloys were 2219 aluminum alloy. After infiltration, the furnace was cooled down to 680 °C in 30 minutes, holding the temperature for other 30 minutes. Then, the application of nitrogen gas was stopped, the derived composites were fetched and cooled down in air. TiN_p/2219 Al composites by pressureless infiltration were obtained.

CLAIMS

1. Method for producing aluminum matrix composites through pressureless infiltration, comprises the steps of:

- preparing, as pre-wettability, a permeable mass/preform comprising at least one type of ceramics reinforcement and aluminum or aluminum alloys powder; and

- communicating reinforcement and aluminium powder to generate a spontaneous infiltration of said permeable mass/preform with molten matrix aluminum or aluminum alloys in a protecting environment at an infiltration temperature without extra pressure.

2. Method according to claim 1, wherein said permeable mass/preform is prepared by a process of cold pressing, hot pressing, tape casting, and the porosity of said permeable mass/preform is lower than 80%.

3. Method according to claim 1 or 2, wherein said reinforcement comprises powders, whiskers, chopped fibers.

4. Method according to claim 1, wherein said ceramics comprise oxides, carbides, nitrides, borides.

5. Method according to claim 1, wherein said ceramics comprise silica, alumina, titanium carbide, silicon carbide, boron carbide, titanium diboride, aluminum boride, magnesium boride, aluminum nitride, titanium nitride, silicon nitride.

6. Method according to claim 1, wherein said protecting environment comprises nitrogen, argon, vacuum atmosphere.

7. Method according to claim 1, wherein the step of preparing as pre-wettability comprises the substeps of:

- weighing the reinforcement;
- weighing the aluminum or aluminum alloys powder;
- mechanically mixing reinforcement and aluminum or aluminum alloys powder;
- making a green preform; and
- heating the green preform in a protecting environment.

8. Method according to claim 7, wherein the step of mechanically mixing is alternatively performed as:

- dry mixing, which generates mixture powders; or

- humid mixing, which generates a mixture with solvent, alternatively subjected to drying to obtain mixture powders or to pressing or tape casting.

9. Method according to claim 7 or 8, comprising then the steps of:

- providing massive aluminum;
- immersing the green preform in an aluminum bath;
- pressureless infiltrating at a temperature ranging between 700 and 1500 °C;
- forming a composite in the aluminum bath;
- extracting the composite and cooling(or cooling within the matrix bath);
- obtaining the composite(or cutting out the composite).

10. Method according to claim 1, wherein the temperature for said spontaneous infiltration is above 650 °C.

11. Method according to claim 1, wherein said permeable mass/preform contains at least 1% in volume of metallic materials.

Fig. 1

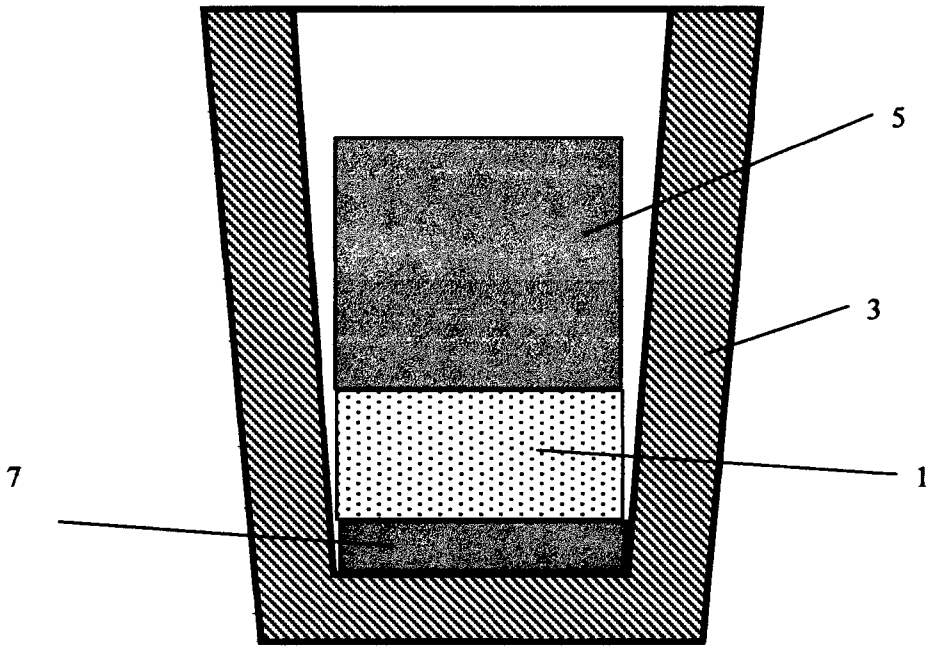


Fig. 2

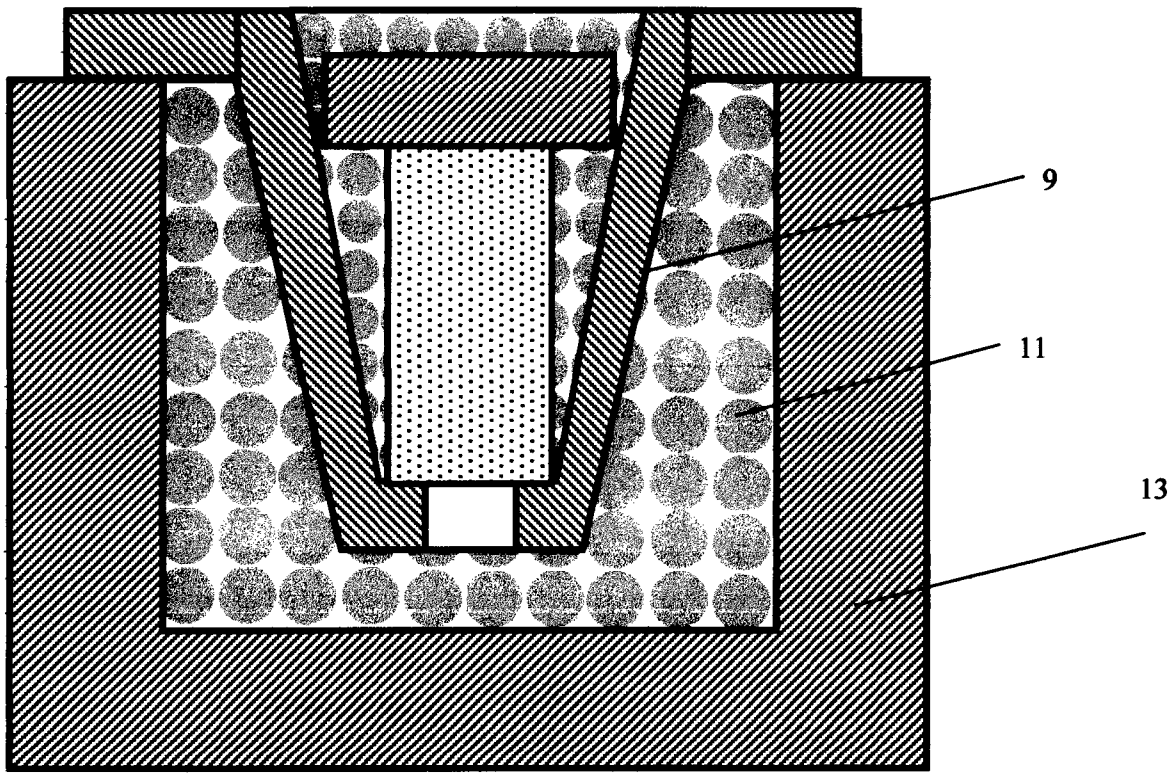
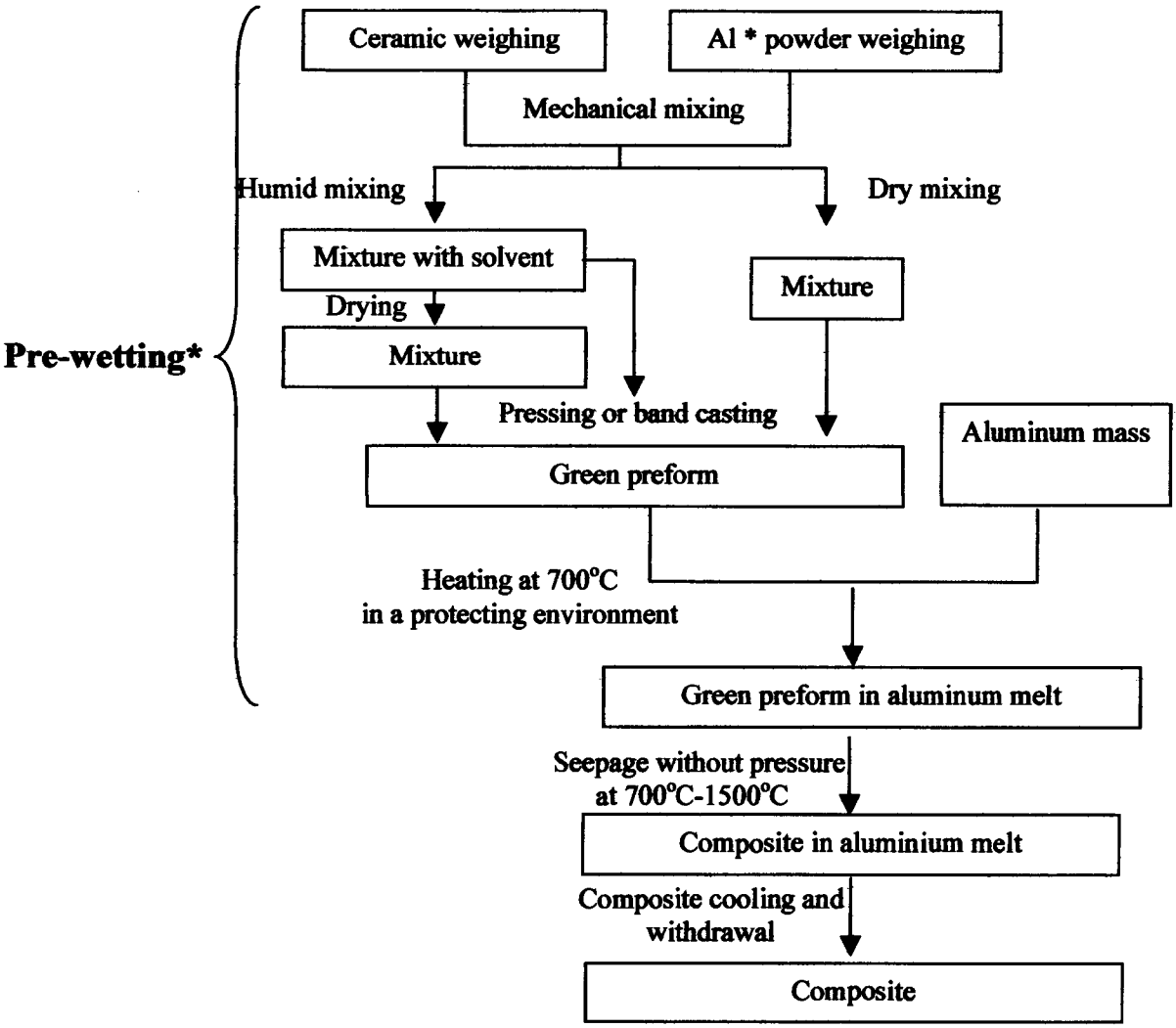


Fig. 3


Pre-wetting*
Ceramic weighing
Al * powder weighing
Mechanical mixing
Humid mixing
Dry mixing
Mixture with solvent
Drying
Mixture
Mixture
Pressing or band casting
Aluminum mass
Green preform
Heating at 700°C
in a protecting environment
Green preform in aluminum melt
Seepage without pressure
at 700°C-1500°C
Composite in aluminium melt
Composite cooling and
withdrawal
Composite

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2014/000168

A. CLASSIFICATION OF SUBJECT MATTER
INV. B05D3/02 C22C29/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B05D C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 626 914 A (RITLAND MARCUS A [US] ET AL) 6 May 1997 (1997-05-06) Abstract; examples 1, 3; claims	1-11
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X	LEE K B ET AL: "Interfacial reactions in SiC P /Al composite fabricated by pressureless infiltration", SCRIPTA MATERIALIA, ELSEVIER, AMSTERDAM, NL, vol. 36, no. 8, 15 April 1997 (1997-04-15) , pages 847-852, XP004324550, ISSN: 1359-6462, DOI: 10.1016/S1359-6462(96)00506-4 p. 847: "Experimental Procedures"	1-11

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2014/000168

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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